



Detoxification of waters contaminated with phenol, formaldehyde and phenol–formaldehyde mixtures using a combination of biological treatments and advanced oxidation techniques

J.A. Ortega Méndez*, J.A. Herrera Melián, J. Araña, J.M. Doña Rodríguez, O. González Díaz, J. Pérez Peña

Centro Instrumental Físico–Químico para el desarrollo de Investigación Aplicada (CIDIA-FEAM), Departamento de Química, Universidad de Las Palmas de Gran Canaria, Edificio Polivalente I del Parque Científico Tecnológico, Campus de Tafira, 35017 Las Palmas de Gran Canaria, Spain

ARTICLE INFO

Article history:

Received 24 March 2014
Received in revised form 10 July 2014
Accepted 15 July 2014
Available online 23 July 2014

Keywords:

Phenol
Formaldehyde
Biological treatment
Advanced oxidation process
Combination

ABSTRACT

The detoxification process of waters contaminated with phenol, formaldehyde and phenol–formaldehyde mixtures was studied using advanced oxidation treatments (heterogeneous photocatalysis and Fenton), biological techniques (aerated biological and wetland reactors) and combinations of the two. It is shown that photocatalysis was efficient in the detoxification of concentrations below 50 mg L^{-1} of those compounds. Sample toxicity increased at higher concentrations due to the generated intermediates. Phenol–formaldehyde mixtures were impossible to detoxify by heterogeneous photocatalysis at any of the studied concentrations. Treatments using the Fenton reaction were able to degrade concentrations above 1000 mg L^{-1} , though the use of a reagent such as peroxide makes it a costly technique. The efficiency of the biological aerated filter (BAF) mainly depended on initial concentration and toxicity, with removal rates of 3.08 and $0.26 \text{ g L}^{-1} \text{ d}^{-1}$ obtained for phenol and formaldehyde, respectively. Taking into account the results obtained for the treatment of complex phenol–formaldehyde mixtures, the best combination of techniques for the treatment of concentrations found in the industrial wastewater studied in this paper was the Fenton + BAF technique which was able to detoxify phenol–formaldehyde concentrations ($1:1$) of 1000 mg L^{-1} .

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

In recent decades industrial development has become associated with an increasing use of natural available resources. Almost 59% of the water used in developed countries is for industrial purposes and these same countries are responsible for 80% of the world's industrial waste waters. As for the developing countries, 70% of factory-generated effluent is discharged without receiving any sort of treatment, with consequent contamination of the available water resources [1]. There is then a clear need for treatment systems suitable for such contaminated effluents.

One of the main difficulties concerning the treatment of toxic effluents is their variable chemical nature and concentration [2]. Because of the high levels of toxicity and the short- and long-term biological effects legislation is commonly required to govern the discharge of such waste materials. Conventional treatments of

household waste waters are insufficient for these types of effluents which can often create problems for the waste water treatment plant due to the presence of persistent and toxic organic compounds [3]. Treatments specifically designed for those types of industrial effluents tend to be complicated and expensive.

One of the procedures developed over the last decade for the treatment of various organic compounds involves the use of biological aerated filter (BAF) reactors. They basically comprise a submerged bed of particles colonized by different strains of bacteria with a continuous supply of air. They are noted for their high efficiency, small size and low cost [4–6]. This type of reactor has begun to be used for the treatment of various waste materials including tri-nitrophenols [7], trinitrotoluene [8], *n*-alkanes [9], etc.

The other biological treatment considered in this study involves the use of artificial wetlands. The processes involved resemble those found in conventional treatment of waste waters in combination with natural processes such as photosynthesis, assimilation by plants, etc. The main difference is that in conventional treatments the processes take place in different reactors at speeds accelerated by an additional input of energy, whereas in the artificial wetlands

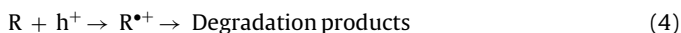
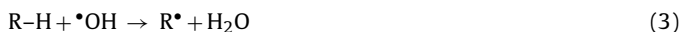
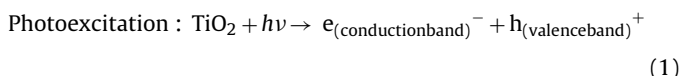
* Corresponding author. Tel.: +34 928 45 73 01; fax: +34 928457397.
E-mail address: jaortegamendez@gmail.com (J.A.O. Méndez).

all the processes occur in a single-system reactor at natural speed. The main advantage of biological systems is their low cost and maintenance requirements [10,11].

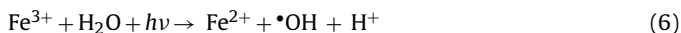
In Nature, biodegradation is the main route of treatment of many xenobiotics though other abiotic processes such as hydrolysis or photolysis can play an important role. The fundamental problem is that many of the compounds present in industrial wastewater are not biodegradable and/or toxic [12].

For the removal of the most resistant compounds one option is the use of the so-called advanced oxidation techniques (AOTs), which are based on the generation of strongly oxidising radicals able to remove or transform these substances into more biodegradable compounds. These techniques include heterogeneous photocatalysis with TiO_2 and homogeneous photocatalysis such as Fenton or photo-Fenton. On occasions, AOTs will give rise to reaction intermediates which are in fact more toxic than the initial compound. This is the case with phenol, whose principal intermediates are hydroquinone and catechol which are much more toxic than phenol itself [13,14].

Heterogeneous photocatalysis is based on the incidence of UV light on a photocatalyst, generally a broad-band semiconductor like titanium dioxide (1). If the radiation has energy equal to or greater than the E_g then an electron is promoted from the valence band to the conduction band, generating an electron–hole pair. This electron–hole pair has to diffuse out to the surface of the photocatalyst before it can intervene in oxidation and reduction reactions that can generate $\bullet\text{OH}$ radicals ((2)–(3)) capable of oxidising the pollutants. The pollutants can also be oxidized directly through the photogenerated holes which diffuse out to the photocatalyst surface (4) [15,16]:



The Fenton reaction (5) consists of a catalytic reaction between the Fe^{2+} and H_2O_2 to generate $\bullet\text{OH}$ radicals. Light can accelerate the process regenerating the Fe^{2+} from the Fe^{3+} formed in the reaction (6). This is known as the photo-Fenton process [17,18].



While many studies in recent years have suggested combining biologically-based techniques and AOTs for optimization of the treatment of a waste material, not only in terms of the removal of the compound but also its complete detoxification, few studies

have in fact been made on such combinations. Those that have been carried out have not taken into account the effect of the presence of various pollutants with different degrees of biodegradability, nor have they considered the case of high concentration levels of one pollutant inhibiting the biodegradation of another [12]. Likewise, studies rarely contemplate the costs involved to show that a particular combination can be considered both innovative and competitive for industrial application [12].

The present paper is based on a study of the removal and detoxification of some of the compounds commonly found in industrial waste waters, namely phenol, formaldehyde and phenol–formaldehyde mixtures (see Table 1), using a combination of biological and photocatalytic treatments which are innovative and economically competitive in comparison with commonly used industrial effluent treatment techniques.

2. Methodology

Phenol (99%) and formaldehyde (35–40%, w/v) were purchased from Aldrich and Panreac respectively. All reagents were of analytical grade.

The photocatalyst used was Evonik P25 TiO_2 (anatase–rutile: 80–20, particle size of 30 nm and BET surface area of $50 \text{ m}^2 \text{ g}^{-1}$). After addition of the photocatalyst (1 g L^{-1}), final pH value was adjusted at the beginning of the reactions to 4.5–5 with sulfuric acid or sodium hydroxide.

For Fenton reactions, high purity $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Panreac) and 35% (w/v) H_2O_2 from Scharlau were used. All experiments were performed without aeration and at pH 3. When necessary, initial pH was adjusted with H_2SO_4 (95–97% Scharlau). At the end of the experiment, catalase from *Micrococcus lysodeikticus* (243,075 U/mL; Fluka) was used to remove the peroxide remaining from the Fenton processes and avoid its interference in the toxicity measurements.

The heterogeneous photocatalytic and Fenton reactors were 250 mL Pyrex cylinders. Aqueous solutions were prepared with Milli-Q water.

The 60 W UV source was a Solarium Philips HB175 UV set of lamps, comprising $4 \times 15 \text{ W}$ Philips CLEO fluorescent tubes (emission spectrum from 300 to 400 nm, maximum at 365 nm), which gave an irradiation level of 8.9 mW cm^{-2} (Graseby 5370 photometer) at a distance of 10 cm.

Total organic carbon (TOC) measurements were made using a Shimadzu 5000-A analyser. Formaldehyde analysis was performed by the chromotropic acid method [19] which gave a detection limit of 3 mg L^{-1} .

Remaining phenolic compounds concentrations at different reaction times were HPLC measured with a Supelco Discovery C18

Table 1
Main characteristics of the compounds used in this study.

Compound	Industrial process	Untreated effluent concentration [mg L^{-1}]	Toxicity [EC_{50} , mg L^{-1}]	Maximum legal discharge concentration
Phenol	Metallurgy Refinery Coal industry	800–8000 [23] 35–1000 [23] 1500–2000 [23]	13.1^a – 510^b [27]	$<0.5 \mu\text{g L}^{-1}$ [28]
Formaldehyde	Adhesives Resins	220–4000 [24] 500–1300 [25,26]	5.8^c – 34.1^d [27]	1 mg L^{-1} [29]
Resins (Mixtures)	Resins	Phenol: 600–2000 [26] Formaldehyde: 500–1300 [26]	–	–

^a Fish (48 h).

^b Mixed bacterial culture (120 h).

^c Crustacea (48 h).

^d Mixed bacterial culture (120 h).

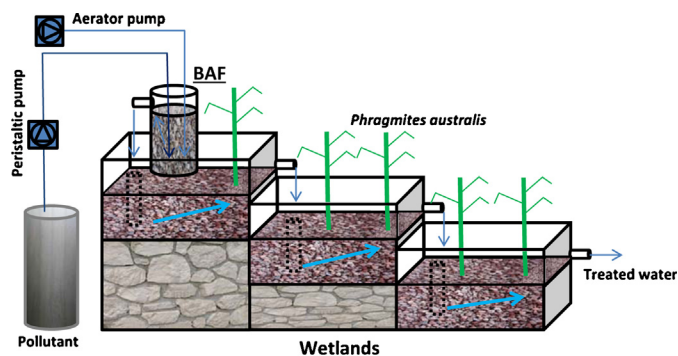


Fig. 1. Representation of the biological system (BAF + wetland) used in the treatment of the different compounds.

(25 cm × 4.6 mm, 5 μm) column and acetonitrile–water–acetic acid (40:59.5:0.5) mobile phase, using a UV detector ($\lambda = 270$ nm).

Toxicity was determined by the *Lemna minor* toxicity test [20]. Glass Petri dishes containing 13 ± 2 fronds of common duckweed (*L. minor*) were placed under constant visible radiation (1×18 W fluorescent tube placed approximately 25 cm above the test chamber) for 96 ± 2 h in a chamber with an ambient temperature of 23 ± 1 °C. Four replicates were used for each sample, i.e., a control without pollutant and samples taken at different reaction times or pollutant concentrations. 15 drops of each concentrated nutrient solution (A, B and C) were added to 50 mL of solution (pollutant aliquots and control). 10 mL of sample at pH 7.5–8 were added to each dish. Growth inhibition percentage (I) was calculated with respect to the control without pollutant (C) and with the pollutant (T) according to:

$$I(\%) = \frac{(C - T)}{C} \times 100 \quad (7)$$

The BAF consisted of a 5 L plastic container (22 cm × 15 cm × 11 cm) filled with gravel to which partially treated urban wastewater was added as seed. The gravel (mean diameter: 3–5 cm) consisted of local crushed volcanic rock. Total surface area [21] of the reactor bed was calculated to be 0.75 m². 100 mL of sludge (TSS: 243 ± 106 mg L⁻¹, no. of data: 43) was added at the beginning of the experiments to speed up bacterial colonization of the gravel. The sludge consisted of shoreline soil obtained from a wastewater treatment pond at the university Campus de Tarifa (Las Palmas de Gran Canaria University). The experiments were initiated 24 h after addition of the sludge and were performed continuously. No further sludge was added. A peristaltic pump was used with flow rate set at 35 ± 5 mL min⁻¹. Formaldehyde and phenol loads were progressively increased by augmenting the amount of both compounds in the influent. The reactor was aerated from below with diffusers using an air pump at a verified flow of 300 mL min⁻¹ (Intelligent Digital Flowmeter, Varian US021 21324).

Wetland experiments were performed in three plastic containers (55 cm × 33 cm × 30 cm) in cascade. Each container was filled with gravel up to 22 cm (46 kg) and partially treated wastewater from the Campus was used as bacterial seed and nutrient source. Six mats made from common reed (*Phragmites australis*) were placed in each reactor. Total water volume was 21 L. Total reactor bed surface area [21] was calculated to be 3 m².

A fitting scheme biological reactor system with the BAF and wetland reactors can be seen in Fig. 1.

Hydraulic residence time (HRT) for the BAF and wetland reactors was calculated using the methodology proposed by Persson et al. [22], with respective obtained times of 54 min and 46 h.

3. Results and discussion

3.1. Toxicity

Table 1 shows the concentrations of phenol and formaldehyde commonly found in wastewaters from different industrial processes [23–26]. Concentrations are commonly over 1000 mg L⁻¹ in the case of both phenol and formaldehyde. Also shown are the toxicity data found in the bibliography using different organisms for the toxicity tests [27] and, finally, the EPA maximum permitted legal concentrations when the waste water is discharged [28,29].

The results of the *L. minor* toxicity test performed on the various compounds under study are shown in Fig. 2A. Formaldehyde was the most toxic of the compounds. At formaldehyde concentrations above 10 mg L⁻¹ growth inhibition levels of over 40% were observed. For phenol, the compound begins to have toxicity values above 50 percent inhibition at concentrations over 250 mg L⁻¹ (TOC₀). Though performed with organisms different to the reference organisms used by Tisler and Zagorc-Koncan [27], the results of the toxicity tests lead to the same conclusion, namely the higher toxicity in all cases of formaldehyde. It was also observed how the main degradation intermediates in the oxidation of phenol, hydroquinone and catechol [16], have higher toxicity levels than those for phenol itself at low concentrations (Fig. 2B), with hydroquinone being the most toxic with over 50% inhibition at concentrations close to 5 mg L⁻¹ (TOC₀). This aspect is important because the technique that is chosen must ensure complete removal of the main compound and the non-generation of these intermediates.

3.2. Heterogeneous photocatalysis

Fig. 3 shows the degradation and mineralization results for the different compounds after 2 h of treatment. Full degradation of phenol was obtained up to concentrations of nearly 50 mg L⁻¹, but process efficiency for formaldehyde began to fall at concentrations as low as 10 mg L⁻¹. Significantly, degradation efficiencies are much lower with the phenol–formaldehyde mixtures than the individual compounds, with degradation efficiencies falling by 50% at concentrations above 50 mg L⁻¹. This indicates a process of simultaneous inhibition.

The role played by methanol needs to be considered in the cases of degradation of formaldehyde and the phenol–formaldehyde mixtures. Methanol is used as a stabilizing chemical compound for formaldehyde (generally at around 11–14%). When methanol is found in high amounts it can react with the holes of the catalyst inhibiting the production of hydroxyl radicals and causing a reduction in formaldehyde degradation [30,31]. For this reason, some authors [32] propose the addition of H₂O₂ in photocatalysis processes with formaldehyde in order to improve degradation efficiency with the formation of •OH radicals.

Previous studies [33] by our group have shown how both formaldehyde and methanol can slow down phenol degradation. Though, as commented previously, methanol acts as a scavenger of •OH radicals involved in phenol degradation, little is known about how formaldehyde behaves in phenol degradation. In the same studies [33], it was observed through FTIR analysis how phenol and formaldehyde can interact on the catalyst surface forming 4-hydroxybenzaldehyde, which may be the cause of the slowing down of phenol and formaldehyde degradation. It was also observed how dosing (adding small volumes of the pollutants to the reactor instead of treating the concentrated sample) the phenol–formaldehyde mixture improved degradation by decreasing the interaction of these compounds with the catalyst surface and therefore reducing the formation of 4-hydroxybenzaldehyde.

As for mineralization of the different compounds, a loss of process efficiency can be observed at concentrations above 50 mg L⁻¹,

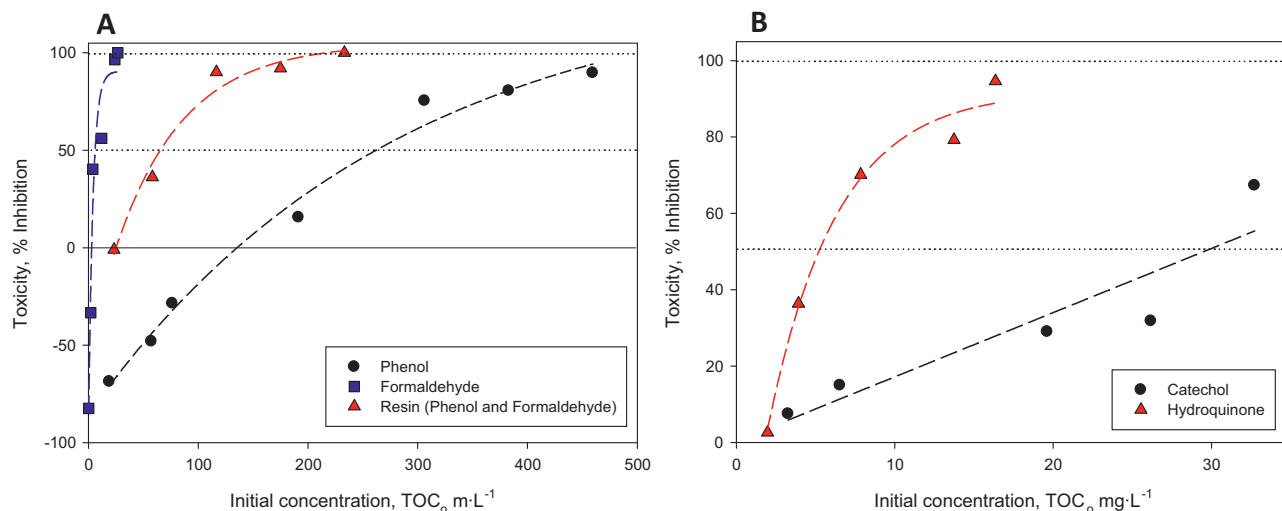


Fig. 2. (A) Toxicities using the *L. minor* test for phenol, formaldehyde and phenol–formaldehyde mixtures (1:1) vs. initial carbon concentration (TOCo). (B) Toxicity of the main phenol degradation intermediates (hydroquinone and catechol).

where generation of the different degradation intermediates begins to have relatively significant concentrations.

Fig. 4A shows the increase in concentrations of phenol intermediates (hydroquinone and catechol) for different initial phenol concentrations after 2 h of treatment. This increase affects not only the mineralization rate but also effluent toxicity at the end of the treatment. During photocatalytic oxidation the concentration of organic substrates over time is dependent upon photonic efficiency. At high substrate concentrations however, photonic efficiency diminishes and the titanium dioxide surface becomes saturated leading to catalyst deactivation [34,35]. Fig. 4B shows how the corresponding hydroquinone and catechol concentrations for the phenol–formaldehyde mixture are much lower. This seems to indicate that degradation of all the phenol is not taking place and that it may be reacting with the formaldehyde, impeding its degradation and so reducing intermediate formation. As for the TiO₂ photodegradation mechanism, various authors [34,35] have proposed that •OH radicals are attacking the phenol ring, generating derivatives such as catechol, resorcinol and hydroquinone. The phenolic rings of these compounds then break down to give malonic acid and, subsequently, short-chain organic acids (such as maleic, oxalic, acetic or formic) and, finally, CO₂. Clearly, full

decomposition of the compound to CO₂ and H₂O will depend on innumerable variables including, amongst others, initial concentration, reaction time, pH, catalyst load and the presence of O₂ [16]. Low mineralization is seen in the case of the phenol–formaldehyde mixtures (1:1) starting at concentrations of 20 mg·L⁻¹. Mineralization in the case of the phenol–formaldehyde mixture decreases linearly with the increase in its concentration.

Fig. 5A shows the evolution of toxicity. It can be seen how full sample detoxification is obtained at initial concentrations below 50 mg·L⁻¹ for phenol and 10 mg·L⁻¹ for formaldehyde and the phenol–formaldehyde mixtures. At higher initial concentrations, final toxicity after the treatment increases, with toxicity values that can be even higher than those of the starting solution. As can be seen in Fig. 5B, the main reason for this increase can be explained by the presence of intermediates, in this case catechol and hydroquinone, which have higher toxicity levels at low concentrations. In addition, it can be seen how the toxicity line has practically the same evolution as the line that marks hydroquinone toxicity.

The effect of the intermediates appears to be an important problem as it not only influences toxicity but also interaction with the catalyst, resulting in a loss of catalyst efficiency. It should be commented that lower concentrations of reaction

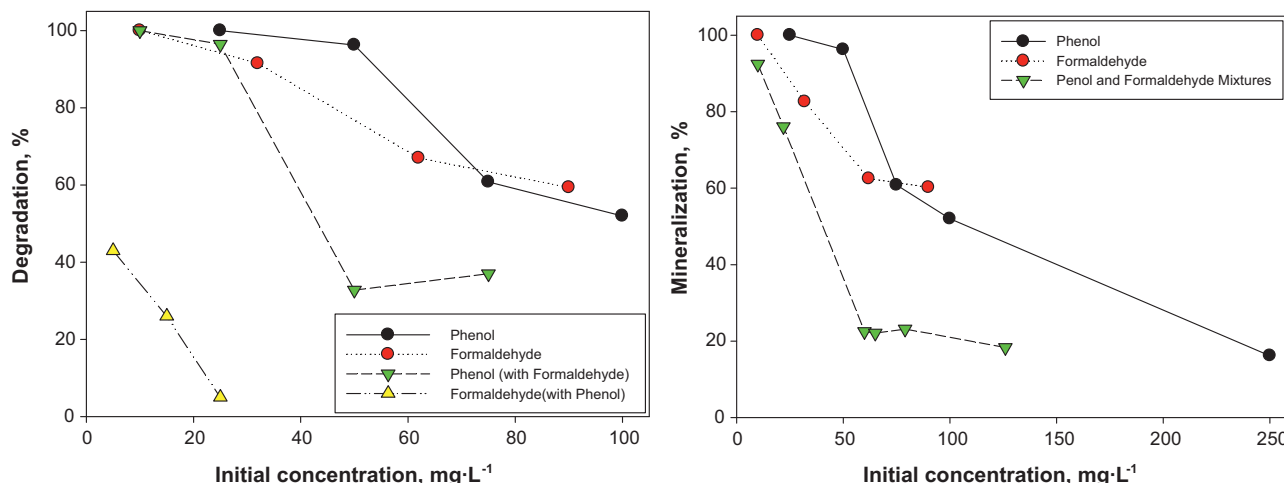


Fig. 3. Percentages of degradation and mineralization of phenol, formaldehyde and phenol–formaldehyde mixtures (1:1) through photocatalysis with TiO₂.

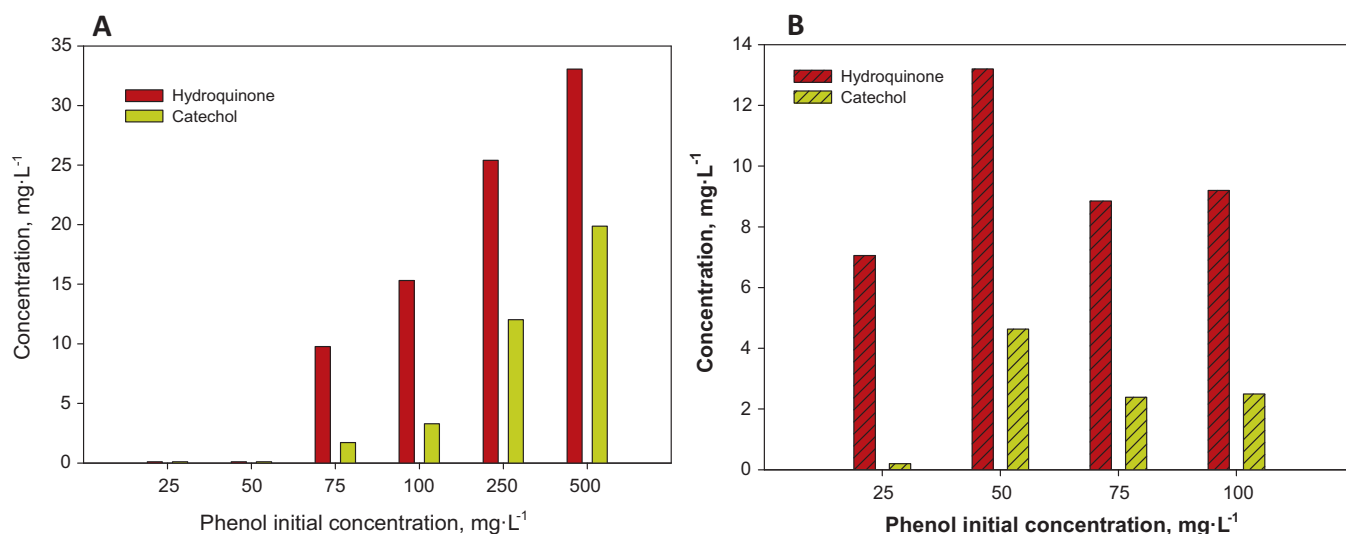


Fig. 4. Concentrations of the intermediates, hydroquinone and catechol, at the end of the treatment (120 min) from different initial concentrations of (A) phenol alone and (B) in combination with formaldehyde (1:1).

by-products have been observed when using other TiO₂ catalysts such as the Sachtleben Hombikat UV 100, as well as less inhibitory effects between the intermediates and the product for degradation [36,37].

3.3. Homogeneous photocatalysis

Preliminary experiments with 75 mg L⁻¹ of phenol and formaldehyde were performed to optimize the Fe²⁺/H₂O₂ molar ratios to achieve the highest degrees of degradation, mineralization and detoxification.

3.3.1. Degradation of phenol with Fenton

Fig. 6A shows the evolution of the concentration, mineralization and toxicity of phenol according to the Fe²⁺/H₂O₂ proportions studied. High percentages of degradation and mineralization were only obtained only for Fe²⁺/H₂O₂ molar ratios above 1:43 (H₂O₂ = 61 mg L⁻¹). With lower concentrations of the peroxide the intermediates were not degraded and toxicity increased.

3.3.2. Degradation of formaldehyde with Fenton

The complete detoxification of formaldehyde was not possible with Fenton (Fig. 6B). Toxicity values were always above 70% inhibition, mainly due to the remaining formaldehyde in the effluent at the end of the treatment. The lower activation energy of formic acid, one of the formaldehyde degradation intermediates [38–40] can be the cause of the low mineralization observed.

3.3.3. Degradation of phenol–formaldehyde mixtures with Fenton

Fig. 6C shows the results for the Fenton treatment of the phenol–formaldehyde mixtures (75 mg L⁻¹:75 mg L⁻¹). For all studied Fe²⁺/H₂O₂ ratios, full degradation was only observed for the phenol. For the formaldehyde, degradation and mineralization percentages above 70% were observed for ratios above 1:57 (H₂O₂ = 1206 mg L⁻¹). Complete detoxification of the effluent was not observed, but values below 50 percent inhibition were obtained above ratios of 1:3 (H₂O₂ = 24 mg L⁻¹). The low toxicity values may be related in part to the low formation of phenol intermediates as commented previously and an inhibitory effect from the interaction between phenol and formaldehyde molecules

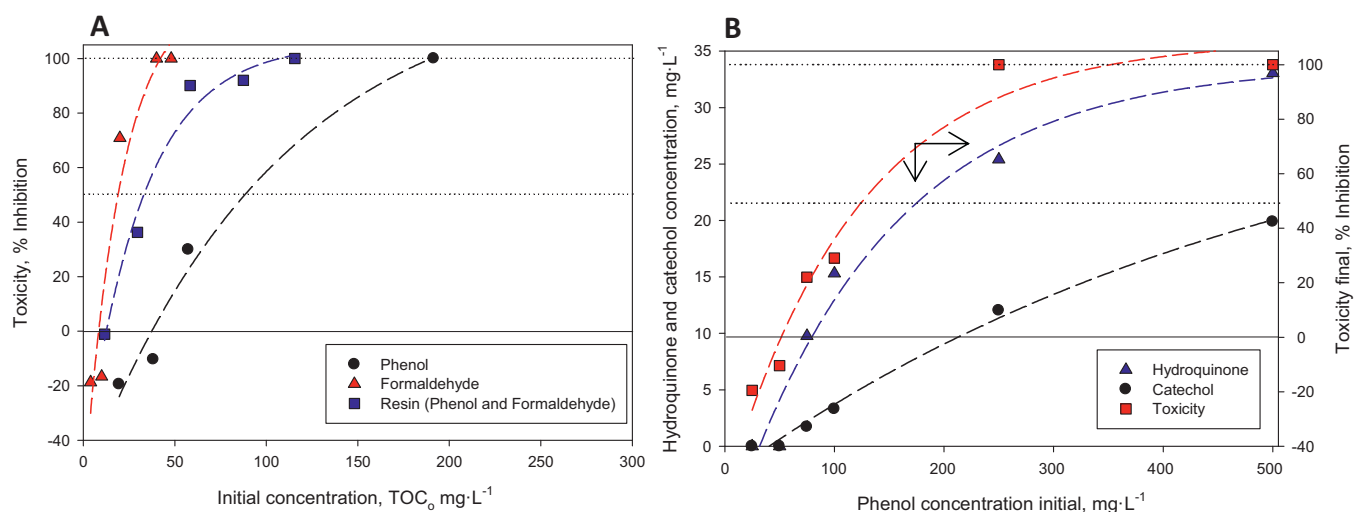


Fig. 5. (A) Toxicities for different initial concentrations after 2 h of treatment. (B) Intermediate concentrations after the tests with phenol and evolution of final toxicity after 2 h of treatment.

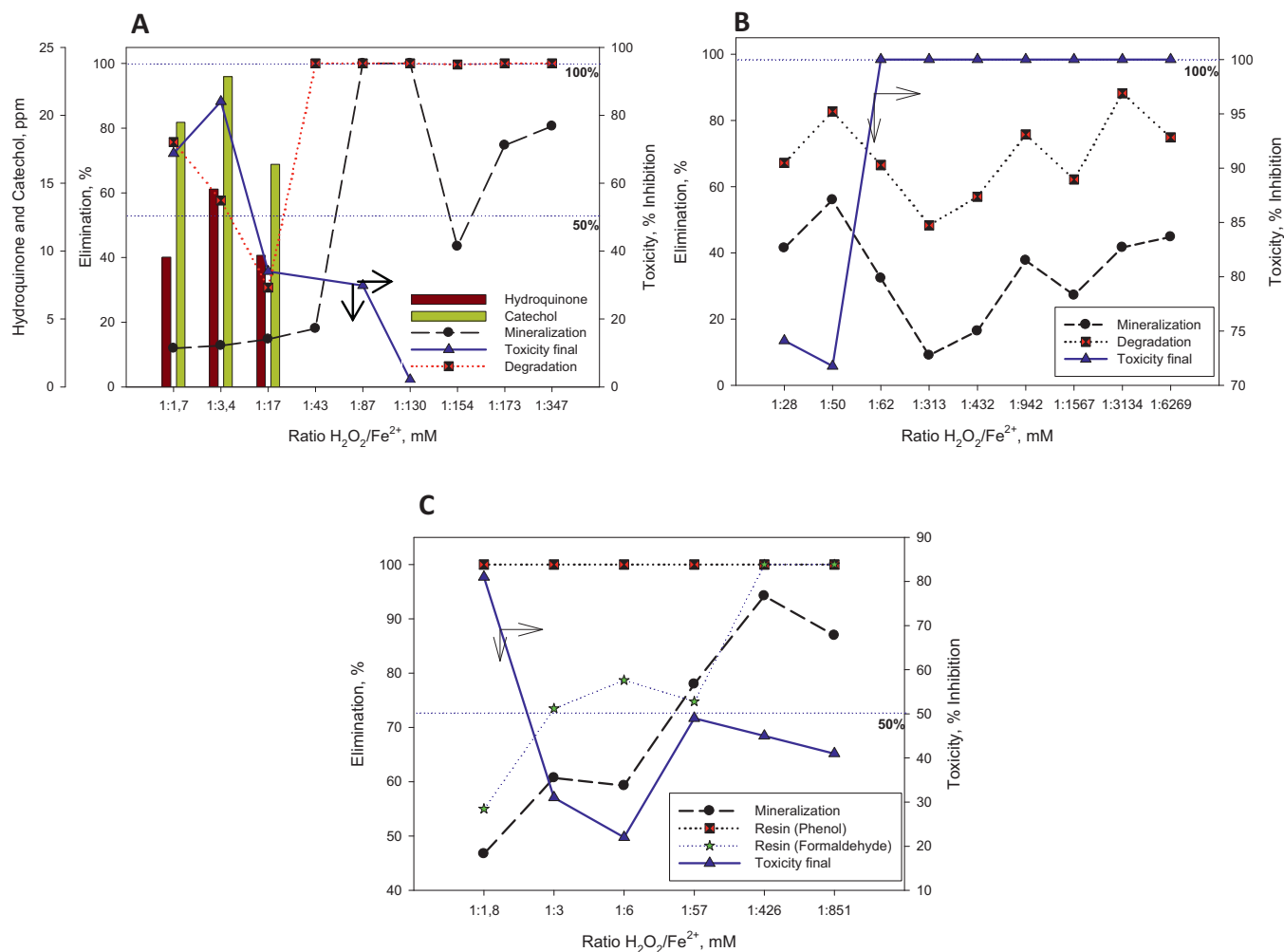


Fig. 6. (A) Phenol (75 mg L⁻¹): degradation, mineralization and final toxicity using Fenton process; final hydroquinone and catechol concentrations. (B) Formaldehyde (75 mg L⁻¹): degradation, mineralization and final toxicity using Fenton process. (C) Formaldehyde-phenol mixture (75 mg L⁻¹:75 mg L⁻¹): degradation, mineralization and final toxicity.

which, when 4-hydroxybenzaldehyde is formed, causes a reduction in toxicity of the formaldehyde which would otherwise not occur if the formaldehyde were alone in the effluent. These experiments have been repeated under irradiation without any further improvement.

Experiments with higher concentrations of phenol, formaldehyde and their mixtures (250, 500 and 1000–1000 mg L⁻¹) were performed. The concentrations of Fe²⁺ and H₂O₂ employed were Fe²⁺/H₂O₂ ratio 1:14 (H₂O₂ = 242 mg L⁻¹) in phenol and formaldehyde and 1:426 (H₂O₂ = 2056 mg L⁻¹) in their mixtures. These reagent concentrations and proportions were determined considering the previous results with lower concentrations of the pollutants. At high concentrations, phenol was always completely degraded but toxicity remained high (100%) because of the presence of intermediates. In fact, the complete removal of organic matter was never achieved in these studies (Fig. 7). Nevertheless, in the experiments with formaldehyde alone degradation and mineralization were above 95% and toxicity was nil with all the concentrations tested.

These results show the Fenton reaction to be a very satisfactory technique for the treatment of those pollutants at relatively high concentrations. However, it was observed that high concentrations of phenol generate toxic intermediates that were not removed with this technique. In fact, the results do not differ greatly from those found in the literature for the removal, for example, of acetaminophen (50 mg L⁻¹) with dosages of H₂O₂ that vary from

575 to 726 mg L⁻¹ [41] with 80% mineralization, or for the removal of a pesticide combination (TOC = 500 mg L⁻¹) with a dosage of H₂O₂ approaching 990 mg L⁻¹ with 40% mineralization [42]. Those data suggest that while the treatment may be very effective in most

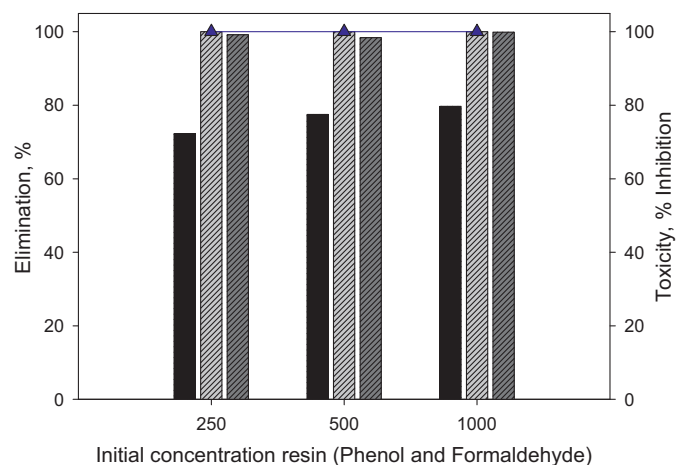


Fig. 7. (A) Fenton at high phenol concentrations and final toxicity (■ TOC; ■ phenol; ▲ toxicity; ● hydroquinone; ▼ catechol). (B) Formaldehyde and final toxicity (■ TOC; ■ formaldehyde; ▲ toxicity). (C) Phenol-formaldehyde mixtures and final toxicity (■ TOC; ■ phenol; ■ formaldehyde; ▲ toxicity).

Table 2

Concentrations and maximum loads using BAF and wetland technique to obtain 100% degradation, mineralization and detoxification.

Treatment	Compounds			
	Phenol	Formaldehyde	Mixtures (phenol)	Mixtures (formaldehyde)
BAF ^a Max (mg L ⁻¹)	200	30.2	100	25
BAF + wetland ^a Max (mg L ⁻¹)	600	199	200	50
Eliminated load ^b Max (g L ⁻¹ d ⁻¹)	3.08	0.26	0.75	0.19

^a Maximum concentration that can be treated without the compound appearing in the effluent.^b Load treated for a BAF system in relation to the eliminated concentration without the compound appearing in the effluent.

cases, the high consumption of H₂O₂ would entail a correspondingly high economic cost.

3.4. Biological reactors

It should be noted that, unlike the experiments with the AOTs, the tests with the biological reactors were performed in continuous mode. Thus, in addition to influent concentration, it was necessary to consider volumetric organic load in the BAF and surface organic load in the wetland.

Table 2 shows the maximum initial concentrations of the compounds that the BAF and wetland process were able to remove completely. When those molecules are found separately, the maximum concentrations for phenol and formaldehyde are 200 and

30.2 mg L⁻¹, respectively, the equivalent of a load of 3.08 and 0.26 g L⁻¹ d⁻¹, respectively. When those compounds are found in a mixture, they both have low rate degradation constants. In the case of phenol, the degradation constant falls by half when the phenol is in a mixture with formaldehyde, while formaldehyde has the same order of degradation as when it is alone in the medium without phenol. It should also be noted that the combination of a BAF and a wetland system would considerably improve the treatable concentrations.

The removal of phenol and formaldehyde when present individually and as a mixture is shown in Fig. 8A and B. For phenol alone in the medium, an effective phenol removal of above 95% was obtained for loads close to 2.84 g L⁻¹ d⁻¹. This efficiency falls by half in the presence of formaldehyde to 1.42 g L⁻¹ d⁻¹ (50%).

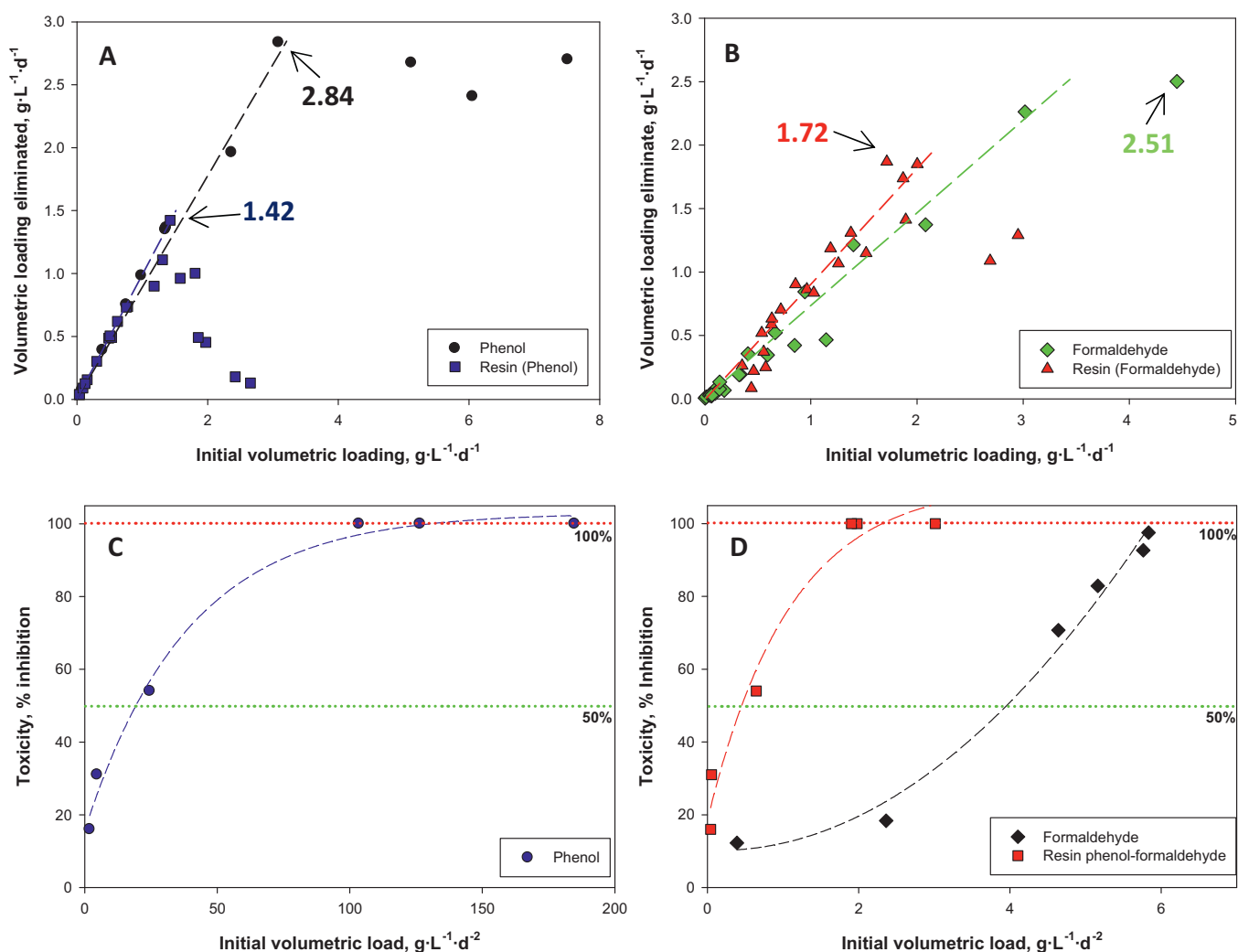


Fig. 8. Biological treatments comparing each compound alone and in the presence of the other (as resin) for (A) phenol, (B) formaldehyde and (C) toxicities at end of treatment for phenol and (D) toxicities at end of treatment for formaldehyde and phenol-formaldehyde mixture.

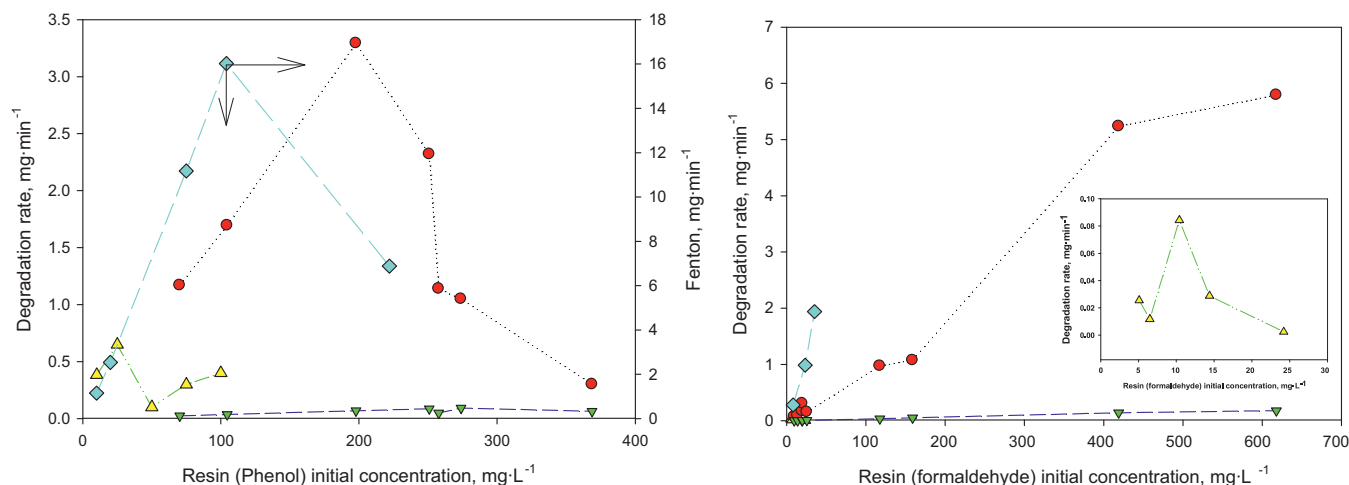


Fig. 9. Degradation and mineralization rates for the different compounds in the phenol–formaldehyde mixtures (● BAF, ◆ Fenton, ▲ photocatalysis, ▼ wetland).

The presence or otherwise of phenol in mixture had less effect on formaldehyde degradation results. Degradation was achieved of loads close to $2.51 \text{ g L}^{-1} \text{ d}^{-1}$ in the case of formaldehyde alone in the medium and of up to $1.72 \text{ g L}^{-1} \text{ d}^{-1}$ (31%) when combined with phenol.

As for effluent detoxification after the BAF treatment, it was observed that final toxicity values were above 50% inhibition for the phenol at initial volumetric loads above $25 \text{ g L}^{-1} \text{ d}^{-1}$. For the formaldehyde and phenol–formaldehyde mixture, the effluent had high toxicity at relatively low input loads of 1 and $4 \text{ g L}^{-1} \text{ d}^{-1}$, respectively, with 100% inhibition observed for initial loads of $2 \text{ g L}^{-1} \text{ d}^{-1}$ of the phenol–formaldehyde mixture.

Degradation efficiencies vary when formaldehyde is or is not present in mixture by $3 \text{ g L}^{-1} \text{ d}^{-1}$ of initial phenol load. However, in the presence of formaldehyde high rates of phenol removal efficiency were observed at much lower loads of around $1 \text{ g L}^{-1} \text{ d}^{-1}$. It should be remembered that in this interval the reactor is receiving a mean formaldehyde dosage of $0.9 \text{ g L}^{-1} \text{ d}^{-1}$, but that this ranges between 0 and $4.96 \text{ g L}^{-1} \text{ d}^{-1}$. These values are in line with those obtained by other authors with loads treated for phenol–formaldehyde mixtures of $1.2 \text{ g L}^{-1} \text{ d}^{-1}$ using moving-bed sequential continuous-inflow reactors (MSCR) [43]. Those results show the capacity of these systems to remove phenol even when another compound is present in the medium. Similar conclusions were obtained in other studies [44] on the degradation of different phenol concentrations of $250\text{--}4000 \text{ mg L}^{-1}$ (from 0.04 to $0.59 \text{ kg m}^{-3} \text{ d}^{-1}$) added to industrial wastewater from resin production. Despite the presence of other carbon sources in the wastewater, phenol was completely removed at all concentrations. TOC removal of 91.3% was obtained at a mean organic loading rate

of $0.11 \text{ kg TOC m}^{-3} \text{ d}^{-1}$. So, despite the addition of high concentrations of phenol, TOC removal efficiency was very high.

Very few studies have been found in the literature consulted by the present authors on the effect of the presence of phenol on formaldehyde degradation and vice-versa [43,44]. The results obtained show an effective formaldehyde load of $0.01\text{--}0.07 \text{ g L}^{-1} \text{ d}^{-1}$. Differences in the results can be found between different studies performed with different reactor types; $2.316 \text{ g L}^{-1} \text{ d}^{-1}$ for anaerobic bed bioreactors [25], from 0.08 to $2.78 \text{ g L}^{-1} \text{ d}^{-1}$ for anaerobic sequencing batch biofilm reactors (ASBBR) [45], or the results obtained in the present study of between 0.01 and $0.9 \text{ g L}^{-1} \text{ d}^{-1}$ for a BAF reactor.

Despite the good results obtained in terms of compound degradation, the detoxification results were not as expected. For the case of phenol (Fig. 8C), 100% toxicity was observed for initial volumetric loads of $100 \text{ g L}^{-1} \text{ d}^{-1}$. In the case of formaldehyde and the phenol–formaldehyde mixture (Fig. 8D), the volumetric loads that can be treated to obtain full detoxification of the wastewater were two orders of magnitude lower than for phenol.

3.5. Comparison and economic evaluation of the different methods

Comparing treatment techniques of such different methodologies is complicated. In order to evaluate the effectiveness of any particular technique and reach to a conclusion, it was decided to use and compare the degradation rate obtained for each compound. For estimation of the different degradation rates of the AOTs and discontinuous (batch) biological reactors, the value of the initial rate was used as comparison estimator supposing an apparent

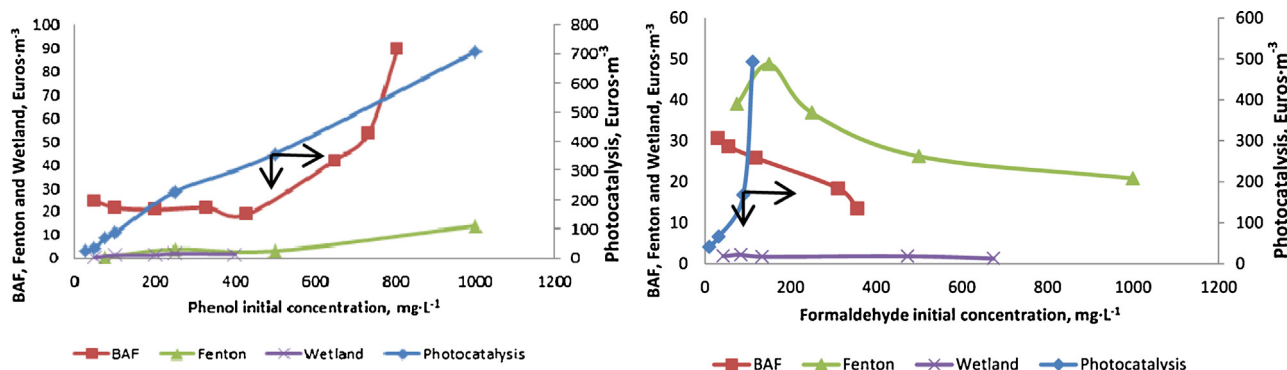


Fig. 10. Economic cost of the different techniques for the two compounds.

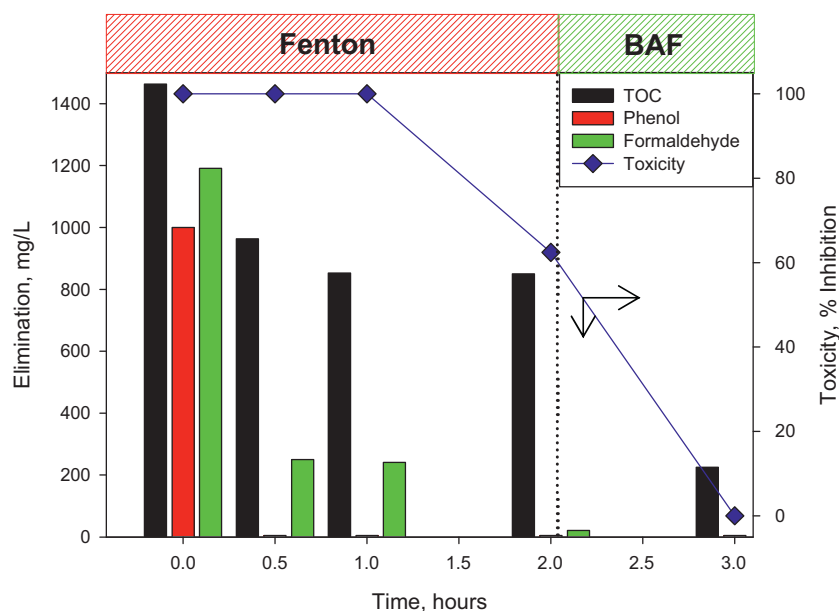


Fig. 11. Combination of a Fenton + BAF treatment for phenol–formaldehyde mixtures (1000 mg L^{-1} : 1200 mg L^{-1}).

first order kinetic behaviour for each initial tested compound concentration. For the continuous biological reactors, the eliminated concentration (initial concentration minus the final concentration) was divided by the HRT_{exp} of each reactor. Fig. 9 shows the results obtained for the degradation rates of each of the compounds in the phenol–formaldehyde mixtures. The wide range of concentrations with high degradation rates when using the BAF treatment should be noted. At low concentrations, $<50 \text{ mg L}^{-1}$, the method with the highest degradation rates was photocatalysis with TiO_2 . However, the Fenton method was the most efficient treatment for degradation of all compounds with much higher degradation rates than the other studied processes.

To determine the economic cost of the different treatment techniques, the methodology proposed by various authors was followed [46,47]. According to these authors, the costs can be estimated based on the rate constants for pollutant degradation.

Eq. (8) was used for cost calculations. Electric energy per order (EE/O) is the electric energy in kilowatt hours [kWh] required to degrade a contaminant by one order of magnitude in a unit volume of contaminated water:

$$\text{EE/O} = \frac{P_{\text{elec}} \cdot t_{90} \cdot 1000}{V \cdot 60 \cdot \log(C_{A0} - C_A)} \quad [46] \quad (8)$$

where P_{elec} is the electric power in kilowatts [kW], V is the treated volume (1 m^3 was assumed), C_{A0} and C_A are the initial and final pollutant concentrations. The value of t , time to achieve 90% degradation was calculated considering the obtained degradation constant according to Eq. (9).

$$t_{90} = \frac{0.9 \cdot C_{A0}}{k} \quad [46] \quad (9)$$

Fig. 10 shows the results obtained for the phenol and formaldehyde treatment costs. It can be seen how in both cases, though even more so in the case of formaldehyde, the cost for the photocatalysis method rises sharply as the concentration increases. The overall cost of these treatments is very influenced by specific costs, including UV lighting, aeration, recirculation, pH adjustment, etc. The most economic treatments for phenol are the Fenton and wetland processes, followed by BAF where the costs rises when treating effluents with concentrations above 400 mg L^{-1} . Wetland treatment is the most economic method for formaldehyde followed

by Fenton and BAF where the cost falls as the concentration rises, with price differences between the two of around 10 euros m^{-3} .

It should be remembered that immediate AOT costs are strongly affected by the cost of the reagents. With the Fenton process, the higher the concentration of contaminants the higher the consumption of reagents, both of iron salts and hydrogen peroxide.

Though it might appear that the Fenton technique can be considered an expensive treatment method due to peroxide consumption, other factors apart from the reagent cost need to be considered when making an overall cost estimation. Those include, as reported by some authors [41] depreciation costs or total water volume treated per year [41].

In the case of photocatalysis with TiO_2 , one of the main consumption costs is the electricity cost for powering the UV lighting source, though this cost could be reduced by using LEDs [48] or solar light [33].

Another important aspect to be taken into consideration is the scalability of the processes. While the tests in the present study were conducted at laboratory scale, it might be assumed that a higher scale would entail a correspondingly higher cost. Studies undertaken combining biological and photo-Fenton processes [42] for pesticide treatment showed that a scaling-up from 1 to $40 \text{ m}^3 \text{ d}^{-1}$ would in fact entail a cost saving of up to 50% for the biological process and of up to 30% for the photo-Fenton. This is because the photo-Fenton process acts as a pre-treatment which totally or partially oxidises the most resistant compounds making them more biodegradable for the subsequent biological process.

3.6. Combination of AOTs and biological techniques

Though biological treatment is often the most efficient alternative for industrial wastewater treatment, there are serious limitations to it when handling recalcitrant and/or toxic organic substances. The capacity of AOTs to enhance biodegradability of the more recalcitrant or biodegradation-inhibiting compounds justifies their use in combination with biological techniques [12,49–53]. AOTs are essentially more efficient but more expensive than biological methods, which might lead to the conclusion that some combination of the two types of technique could give rise to treatments that are both economical and efficient. Various factors would

need to be investigated including the real overall efficiency of the combination in question, the time required to terminate the combined treatment, the possibility of performing the two treatments at the same time and in an uninterrupted manner, etc. Taking into account the results obtained in this study, the combination was proposed for the treatment of high concentrations of phenol–formaldehyde mixtures. First, Fenton was applied in batch for 2-h with the reagent concentrations already optimized in this study. Then, the so-treated effluent was pumped to the BAF in continuous with a peristaltic pump. Toxicity and the concentrations of phenol, formaldehyde and TOC were analyzed in the Fenton and BAF effluents. Fig. 11 shows the combination for the treatment of a phenol–formaldehyde mixture (phenol 1000 mg L⁻¹, formaldehyde 1200 mg L⁻¹) using the combination of an initial Fenton stage (800 mg L⁻¹ H₂O₂; 0.5 mg L⁻¹ Fe²⁺) and a second BAF stage with continuous flow of 35 mL min⁻¹. After initial two-hour Fenton treatment, phenol and formaldehyde reductions were obtained of 99% and 98%, respectively. However, as mineralization of the compound was no higher than 43.3%, toxicity after this first treatment fell to 62% of inhibition. With the second, BAF, treatment phenol and formaldehyde were fully removed and TOC reduction of 76.5% was achieved. Full detoxification of the effluent was also obtained after the BAF treatment.

Though very few studies have been published on the treatment of real industrial wastewater given the enormous variety of compounds and their different toxicities, there are a few examples of the potential benefits of the combination of those types of techniques for similar waters containing herbicides or pesticides or so-called emerging pollutants [12,49–53]. An inverted combination of first BAF followed by Fenton could also be efficient, provided initial phenol and formaldehyde concentrations are no higher than 100 and 50 mg L⁻¹, respectively, due to the toxicity of the formaldehyde mainly in the biological treatment. In the case of using higher concentrations lower flow rates would be required of 5 mL min⁻¹ to ensure efficiency.

In view of the results, it would seem logical to think that a combination of techniques is the best option for the treatment of different waste materials. On the one hand, AOTs can be used for efficient treatment of almost all types of wastes and concentrations. The main drawbacks of AOTs are the cost of reagents, with pollutant concentration determining the amount of reagent required, and the generation of intermediates, which on occasions can be more toxic than the initial effluent. The main advantage lies in their capacity to degrade high concentrations of pollutants in a relatively short time interval (minutes to hours).

Biological degradation techniques are much more economic, requiring little maintenance and no need for the use of reagents. The main drawbacks involve the input concentration, which cannot be too high or too toxic for the bacterial community, and the treatment times, which can be from days to weeks.

4. Conclusions

The results obtained in this study for the treatment of phenol, formaldehyde and their mixtures show that:

- TiO₂-photocatalysis, lab-scale BAF and wetlands were efficient only for low concentrations of pollutants (<25 mg L⁻¹).
- Fenton and photo-Fenton were more proficient for high pollutant concentrations (250–1000 ppm) but mineralization and detoxification were low
- Fenton, photo-Fenton and TiO₂-photocatalysis were much more expensive than the biological methods in all the concentration range studied.

Additionally, if the evolution of the parental compounds intermediates, toxicity and economic costs are considered, two categories of technique combinations can be established.

- For phenol, formaldehyde and phenol–formaldehyde (1:1) concentrations between 100 and 500 mg L⁻¹ the optimum system would be photocatalysis with TiO₂ + BAF and a wetland for final detoxification of the residue.
- For concentrations above 500 mg L⁻¹, the best combination would be Fenton + BAF.

Acknowledgments

We are grateful for the funding of the Spanish Ministry of Science and Innovation and the Infrastructure Project UNLP10-3E-726.

References

- [1] World Water Assessment Programme (WWAP), Water for People, Water for Life – UN Report on the Development of Water Resources in the World, UNESCO, France, 2003.
- [2] M.T. Ravanchi, T. Kaghazchi, A. Kargari, *Desalination* 235 (2009) 199–244.
- [3] Didier Robert, Sixto Malato, *Sci. Total Environ.* 291 (2002) 85–97.
- [4] Biplob Kumar Pramanik, Suja Fatihah, Zain Shahrom, Elshafie Ahmed, *J. Eng. Sci.* 7 (2012) 428–446.
- [5] J.A. Herrera Melián, A. Ortega Méndez, J. Araña, O. González Díaz, E. Tello Rendón, *Process Biochem.* 43 (2008) 1432–1435.
- [6] Liping Qiu, Jun Ma, Lixin Zhang, *Desalination* 208 (2007) 73–80.
- [7] Jinyou Shen, Rui He, Hongxia Yu, Lianjun Wang, Jianfa Zhang, Xiuyun Sun, Jiansheng Li, Weiqing Han, Lu Xu, *Bioresour. Technol.* 100 (2009) 1922–1930.
- [8] Zhongyou Wang, Zhengfang Ye, Mohe Zhang, Xue Bai, *Process Biochem.* 45 (2010) 993–1001.
- [9] Xin Zhao, Yanming Wang, Zhengfang Ye, G.L. Alistair, Borthwick, Jinren Ni, *Process Biochem.* 41 (2006) 1475–1483.
- [10] L. Zeng, G.Q. Chen, *Ecol. Model.* 222 (2011) 293–300.
- [11] Cristina Ávila, Carolina Reyes, Josep María Bayona, Joan García, *Water Res.* 47 (2013) 315–325.
- [12] I. Oller, S. Malato, J.A. Sánchez-Pérez, *Sci. Total Environ.* 409 (2011) 4141–4166.
- [13] Renáta Homlok, Erzsébet Takács, László Wojnárovits, *Chemosphere* 91 (2013) 383–389.
- [14] V. Kavitha, K. Palanivelu, *Chemosphere* 55 (2004) 1235–1243.
- [15] Kazuya Nakata, Akira Fujishima, *J. Photochem. Photobiol. C* 13 (2012) 169–189.
- [16] Umar Ibrahim Gaya, Abdul Halim Abdullah, *J. Photochem. Photobiol. C* 9 (2008) 1–12.
- [17] Gislaïne Ghiselli, Wilson F. Jardim, Marta I. Litter, Héctor D. Mansilla, *J. Photochem. Photobiol. A* 167 (2004) 59–67.
- [18] C. Walling, *Acc. Chem. Res.* 8 (1975) 125–131.
- [19] B.W. Bailey, J.M. Rankin, *Anal. Chem.* 43 (1971) 782–784.
- [20] APHA, *Standard Methods for the Examination of Water and Wastewater*, 21st ed. Washington, DC, USA, 2005.
- [21] D. Lyew, J.D. Sheppard, *J. Chem. Technol. Biotechnol.* 70 (1997) 230–233.
- [22] J. Persson, N.L.G. Somes, *Water Sci. Technol.* 40 (1999) 291–300.
- [23] S. Shanmuga Priya, M. Premalatha, N. Anantharaman, *J. Eng. Appl. Sci.* 3 (2008) 36–41.
- [24] Maria Łebkowska, Anna Narożniak-Rutkowska, Elżbieta Pajor, *Bioresour. Technol.* 132 (2013) 78–83.
- [25] S.V.W.B. Oliveira, E.M. Moraes, M.A.T. Adorno, M.B.A. Varesche, E. Foresti, M. Zaiat, *Water Res.* 38 (2004) 1685–1694.
- [26] J. Araña, E. Tello Rendón, J.M. Doña Rodríguez, J.A. Herrera Melián, O. González Díaz, J. Pérez Peña, *Chemosphere* 44 (2001) 1017–1023.
- [27] T. Tisler, J. Zagorc-Koncan, *Water Air Soil Pollut.* 97 (1997) 315–322.
- [28] F.A. Banat, B. Al-Bashir, S. Al-Sheh, O. Hayajneh, *Environ. Pollut.* 107 (2000) 391–398.
- [29] ATSDR, *Public Health Statement for Formaldehyde*, Agency for Toxic Substances and Disease Registry, Atlanta, U.S. Department of Health and Human Services, Research Triangle Park, NC, 2011.
- [30] Chuan-yi Wang, Joseph Rabani, Detlef W. Bahnemann, Jürgen K. Dohrmann, *J. Photochem. Photobiol. A* 148 (2002) 169–176.
- [31] Javier Marugán, Dirk Hufschmidt, María-José López-Muñoz, Volker Selzer, Detlef Bahnemann, *Appl. Catal. B: Environ.* 62 (2006) 201–207.
- [32] J. Araña, J.L. Martínez Nieto, J.A. Herrera Melián, J.M. Doña Rodríguez, O. González Díaz, J. Pérez Peña, O. Bergasa, C. Alvarez, J. Méndez, *Chemosphere* 55 (2004) 893–904.
- [33] J. Araña, J.A. Herrera Melián, J.A. Ortega, J.I. Macías Sánchez, Pérez Peña F.J., *J. Adv. Oxid. Technol.* 11 (2008) 292–299.
- [34] C. Wu, X. Liu, D. Wei, J. Fan, L. Wang, *Water Res.* 35 (2001) 3927–3933.
- [35] K. Ishibashi, A. Fujishima, T. Watanabe, K. Hashimoto, *J. Photochem. Photobiol. A* 134 (2000) 139.
- [36] G. Marci, A. Sclafani, V. Augugliaro, L. Palmisano, M. Schiavello, *J. Photochem. Photobiol. A* 89 (1995) 69–7432.

- [37] W.F. Jardim, S.G. Moraes, M.M.K. Takiyama, *Water Res.* 31 (1997) 1728–1732.
- [38] Puangrat Kajitvichyanukul, Ming-Chun Lu, Aditsuda Jamroensan, *J. Environ. Manage.* 86 (2008) 545–553.
- [39] Xiangxuan Liu, Jiantao Liang, Xuanjun Wang, *Water Environ. Res.* 83 (2011) 418–426.
- [40] Z.H. Wei, *Chin. J. Chem. Eng.* 17 (2003) 667–672.
- [41] Irene Carra, Elisabet Ortega-Gómez, Lucas Santos-Juanes, José Luis Casas López, José Antonio Sánchez Pérez, *Chem. Eng. J.* 224 (2013) 75–81.
- [42] José Antonio Sánchez Pérez, Isabel María Román Sánchez, Irene Carra, Alejandro Cabrera Reina, José Luis Casas López, Sixto Malato, *J. Hazard. Mater.* 244–245 (2013) 195–203.
- [43] Gholamreza Moussavi, Mahdi Heidarizad, *J. Biotechnol.* 150 (2010) 240–245.
- [44] M. Eiroa, A. Vilar, C. Kennes, M.C. Veiga, *Bioresour. Technol.* 99 (2008) 3507–3512.
- [45] N.S. Pereira, M. Zaiat, *J. Hazard. Mater.* 163 (2009) 777–782.
- [46] Naresh N. Mahamuni, Yusuf G. Adewuyi, *Ultrason. Sonochem.* 17 (2010) 990–1003.
- [47] J.R. Bolton, K.G. Bircher, W. Tumas, C.A. Tolman, *Pure Appl. Chem.* 73 (2001) 627–637.
- [48] Z. Wang, J. Liu, Y. Dai, W. Dong, S. Zhang, J. Chen, *J. Hazard. Mater.* 215–216 (2012) 25–31.
- [49] I. Oller, S. Malato, J.A. Sánchez Pérez, W. Gernjak, M.I. Maldonado, L.A. Pérez Estrada, C. Pulgarín, *Catal. Today* 122 (2007) 150–159.
- [50] A. Kyriacou, K.E. Lasaridi, M. Kotsou, C. Balis, G. Pilidis, *Process Biochem.* 40 (2005) 1401–1408.
- [51] M.M. Ballesteros Martín, J.A. Sánchez Pérez, F.G. Fernández, J.L. Casas López, A.M. García-Ripoll, A. Arques, I. Oller, S. Malato Rodríguez, *Chemosphere* 70 (2008) 1476–1483.
- [52] J. Araña, C. Garriga i Cabo, C. Fernández Rodríguez, J.A. Herrera Melián, J.A. Ortega Méndez, J.M. Doña Rodríguez, J. Pérez Peña, *Chemosphere* 71 (2008) 788–794.
- [53] Julia García Montaña, Francesc Torrades, A. José, García-Hortal, Xavier Doménech, José Peral, *Appl. Catal. B: Environ.* 67 (2006) 86–92.